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A DISSERTATION

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
IN THE UNIVERSITY OF MICHIGAN

By
Wallace E. Gordon
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Easton, Pa.
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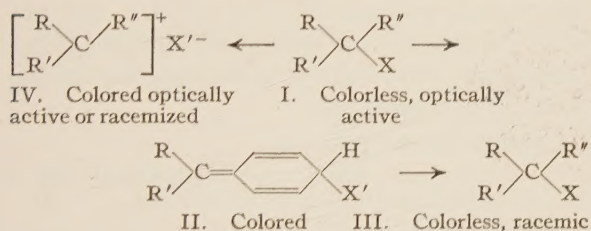


[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Halochromic Salts from Some Triarylmethylthioglycolic Acids¹

BY M. GOMBERG AND W. E. GORDON

Attempts have been made to decide between the benzenoid (carbonium ion) and the quinonoid constitution for triarylmethane dyes² and for the so-called halochromic salts,³ on the basis of the following considerations. A colorless and optically active triarylmethyl compound, when converted into a halochromic derivative and then back again into one that is colorless, does not necessarily become racemized, provided the benzenoid constitution be retained in every stage of the process. If, however, the halochromic compound be quinonoid in structure, then the original compound will have lost in the tautomerization to the quinonoid state the asymmetry of its central carbon atom, and hence on the reverse change to a colorless, again asymmetric, derivative, a racemic compound must inevitably result.



Consequently, if optical activity be maintained through these forward and reverse changes, then definite proof is furnished that quinonoidation could not possibly have occurred. The main obstacle in the prosecution of these studies has been the want of success in resolving the asymmetric compounds chosen. Recently, however, Wallis⁴ accomplished this task in elegant manner. Selecting the same carbinol as has been used by the previous workers, phenylbiphenyl- α -naphthylcarbinol, he combined it with thioglycolic acid and through the brucine salt of the new compound he succeeded in resolving the racemic mixture into its antipodes, each entirely colorless, *d*- and *l*-phenylbiphenyl- α -naphthylmethylthioglycolic

acid, $(\text{C}_6\text{H}_5)(\text{C}_6\text{H}_5\text{C}_6\text{H}_4)(\alpha\text{-C}_{10}\text{H}_7)\text{C-SCH}_2\text{COOH}$. The *l*-acid was found to form halochromic compounds with sulfuric acid and perchloric acid, and with metal halides. When, without previous isolation of the halochromic compound, the deep blue-violet solution which had resulted from the addition of either of the two mineral acids, or of mercuric chloride, was poured into water, the product of hydrolysis was the colorless, racemic, phenyl-biphenyl-naphthylcarbinol, but when the corresponding zinc chloride, or the ferric chloride compound was hydrolyzed, the resulting colorless product was unchanged triarylmethylthioglycolic acid, apparently not even partial racemization taking place. Consequently, it was necessary to infer that the original asymmetric configuration of the colorless mother substance remained undisturbed through the changes, and that optical activity must have been maintained by those two halochromic compounds as such.

Choice of Constitution.—While the behavior of the first three halochromic derivatives was consistent with either quinonoid or benzenoid structure for these, quinonoid structure seemed definitely excluded for the ferric and zinc chloride compounds. However, neither could the alternative, the carbonium ion constitution $(\text{R}_3\text{C})^+\text{X}^-$ ($\text{X}=\text{SCH}_2\text{COOH}.\text{MeCl}_n$), be made to harmonize with the behavior of these two derivatives, specifically in two important respects. (1) Unlike the other three compounds, the last two gave upon hydrolysis not triarylcarbinol but the triarylmethylthioglycolic acid, thus indicating that the C-S linkage in these halochromes is non-ionic. (2) A second reason against considering the zinc and iron compounds as truly carbonium salts is that such a view would imply that in them the optical activity is being maintained by the trivalent cation $\left(\begin{array}{c} \text{R} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{R} \end{array} \right)^+$, wherein the carbon atom possesses only a sextet of valency electrons, unlike the optically stable sulfonium cation $\left(\begin{array}{c} \text{R} \\ \diagup \\ \text{S} \\ \diagdown \\ \text{R} \end{array} \right)^+$. To attribute optical stability, however, to a carbonium cation would be contrary to the recent evidence by Kenyon and Phillips, as Wallis indicated at the time, and as he himself has

(1) From a dissertation by W. E. Gordon, holder of the Monsanto Chemical Works' Fellowship, 1931-1933, submitted to the Faculty of the University of Michigan in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1933.

(2) Meisenheimer and Neresheimer, *Ann.*, **423**, 105 (1921).

(3) G. Karagunis, Ph.D., Dissertation, Freiburg, 1926; H. Krauss, Ph.D. Dissertation, Munich, 1928.

(4) (a) Wallis, *Proc. Nat. Acad. Sci.*, **16**, 215 (1930); (b) *This Journal*, **53**, 2253 (1931); (c) **55**, 3838 (1933).

subsequently so well demonstrated.⁵ And so, in order to cover all the halochromic salts, Wallis finally concluded that "the most likely representation for their structure is $\left[\begin{smallmatrix} R \\ R' \end{smallmatrix} \text{C}-R'' \right] X$, in

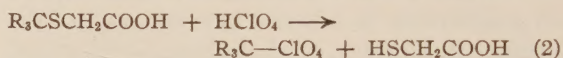
which the central carbon atom is coordinately unsaturated. . . . The C-X bond may or may not be a true ionic linkage," depending on the particular nature of the group X.⁶ The underlying concept is the one not infrequently applied, namely, the shared electron pair in the C:X linkage will in no case be in the middle, *i. e.*, truly homopolar, but will be shifted to a varying extent depending upon the nature of the molecule, and thus the bond may possess varying degrees of polarity.

The above conclusion may hold true in such cases when either the base or the acid radical in a given compound is distinctly different from the corresponding component in another, analogous, compound, or when the two otherwise very similar compounds are placed each under quite unlike experimental conditions, but that conclusion can hardly be applied to the examples under immediate discussion. Here one is to assume from the behavior of the compound $R_3CSCH_2CO_2H \cdot HgCl_2$, that the bond C-S is electrovalent, and from the behavior of the wholly analogous zinc chloride complex, placed under identical experimental conditions that the same bond is not ionic. Evidence,⁷ however, is strongly in favor of the opinion that there is a sharp division between the two kinds of links, and that only in rare instances is the binding force composed of coulombic and covalent force in sufficiently comparable magnitudes to actually permit a ready transition of the compound from ionic to non-ionic behavior. In the words of Sidgwick, "links which are truly intermediate between electrovalence and covalence rarely if ever occur."⁸

The above considerations lead to the conclusion that the various halochromic derivatives, notably those which result from the action of metal halides, may be expected all to exhibit rather similar be-

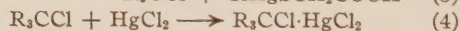
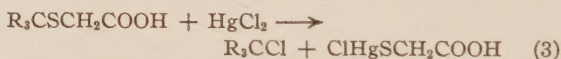
havior as regards optical stability and as regards the nature of the products upon hydrolysis. The actual isolation of the halochromic derivatives as such seemed advisable for the further study of this question.

Triarylmethylthioglycolic Acids are Cleaved by the Halochromizing Agents.—We assume that when speaking of the intensely colored "compounds"⁹ which the triarylmethylthioglycolic acid forms with sulfuric and with perchloric acid, Wallis, like ourselves, has in mind not addition products something like $R_3CSCH_2COOH \cdot HClO_4$, but rather such salts as R_3C-ClO_4 , and the formation of these in accordance with the reaction



If this be their composition, then subsequent hydrolysis must necessarily give rise to triarylcabinol and not to its thioglycolic acid derivative.

The close similarity in behavior of the mercuric chloride derivative to that of the sulfate and perchlorate, suggests that it, too, is likely to be a halochromic compound of the carbinol, and not of its thioglycolic acid derivative, and that it has been produced through a similar reaction mechanism as the perchlorate



It seemed probable that other metal halides, zinc or ferric chloride, would act in this case not differently from mercuric chloride. Unfortunately, this inference could not be verified experimentally on that compound which was used by Wallis.

As a matter of fact, phenylbiphenylnaphthylmethylthioglycolic acid is not suitable for the preparation of the halochromic salts, since the corresponding carbinol chloride itself fails, for reasons given below, to give crystalline double salts with metal halides. Asymmetry playing no part in the cleavage reaction, we selected a series of triarylmethylthioglycolic acids largely on the basis that the corresponding carbinol chlorides if produced would likely form crystalline double salts. The requisite triaryl carbinols were converted into the thioglycolic acid derivatives by following Biilmann's¹⁰ directions for triphenylmethylthioglycolic acid and the yields were uniformly excellent. The acids recrystal-

(5) Kenyon and Phillips, *J. Chem. Soc.*, **133**, 1676 (1925); Wallis and Adams, *THIS JOURNAL*, **55**, 3843 (1933): "It seems probable that only under special conditions (examples mentioned) can triaryl substituted groups . . . maintain even momentarily an asymmetric configuration and, whenever a replacement takes place in such a manner as to involve the intermediate formation of a true carbonium ion racemized products will inevitably result."

(6) The above formulation, it seems to us, fails of its intended purpose, since placing the X in the second sphere of the coordinated complex (R_3C) is to say that it responds to all tests as an ion.

(7) Sidgwick, "The Covalent Link in Chemistry," The Cornell University Press, Ithaca, N. Y., 1933, pp. 30-61.

(8) Ref. 7, p. 61.

(9) Ref. 4b, p. 2255 and p. 2260.

(10) Biilmann and Due, *Bull. soc. chim.*, **35**, 386 (1924).

lized from toluene and from glacial acetic acid were colorless and were shown by analysis to be pure.

In the preparation of the metal halide derivatives, best yields were obtained when glacial acetic acid containing a small amount of acetic anhydride was used as solvent. In some instances ether or ether-benzene mixtures were employed, and then it was necessary to wash the crystalline material thoroughly with cold acetic acid in order to remove the metal salt of thioglycolic acid which is produced in the reaction (Equations 3 and 4), and which is insoluble in ether or ether-benzene mixtures. Best yields of the double salts were obtained when two and one-half moles of the metal halide were used for each mole of the thioglycolic acid derivative. Ordinarily we used 1.0 g. of the triarylmethylthioglycolic acid dissolved in 20 to 50 cc. of the solvent, and the metal halide in more concentrated solutions. Separation of the double salt, yellow to deep crimson in color, commences within a few minutes to several hours, varying with the individual compounds and with the nature of the solvent employed. The double salts so formed were compared with the salts prepared directly from the union of the corresponding triarylcarbinol chlorides and the metal halide, and were found to agree with these in every respect. Upon hydrolysis they all yielded triarylcarbinol in the calculated amounts. The

from the two halochromic salts contained thioglycolic acid or its salt, respectively. The acid was extracted from its aqueous solution by ether, and the identification was done through the characteristic barium and barium-zinc salts.¹¹

Secondary Changes when a Naphthyl Group is Present in the Molecule.—It has been shown by Ullmann¹² that diphenyl- α -naphthylcarbinol or the carbinol chloride, and by Schoepfle¹³ that the phenyldinaphthyl compounds undergo readily fluorene formation, the reaction being catalyzed by the addition of a little mineral acid or zinc chloride to the acetic acid solution of the carbinol. The addition of metal halide produces indeed an intense coloration, but crystallization of the double salt is hindered by the secondary change, either in the carbinol halide or in the double salt, which sets in at once and proceeds continuously to completion.

Obviously, a similar course of reaction is to be expected when one starts with the thioglycolic acid derivative instead of with the carbinol chloride. Such, we found, is the case with diphenyl-

TABLE I

CLEAVAGE OF TRIARYLMETHYLTHIOGLYCOLIC ACID DERIVATIVES BY METAL HALIDES AND BY PERCHLORIC ACID

No.	(R ₃ C)SCH ₂ COOH acid	M. p., °C.	Agency causing cleavage	Formula	The halochromic product			
					Chlorine, %		Metal, %	
					Calcd.	Found	Calcd.	Found
1	Tri- <i>p</i> -tolylmethyl-	185	Zinc chloride	(C ₇ H ₇) ₃ CCl·ZnCl ₂	23.28	23.02	14.31	13.83
			Ferric chloride	(C ₇ H ₇) ₃ CCl·FeCl ₃	29.40	29.24	11.59	11.68
2	Phenylxanthenyl- ^a	173	Zinc chloride	C ₁₈ H ₁₈ OC·ZnCl ₂	24.80	24.56	15.24	15.10
			Ferric chloride	C ₁₈ H ₁₈ OC·FeCl ₃	31.18	30.79	12.28	11.97
			Stannic chloride	C ₁₈ H ₁₈ OC·SnCl ₄	32.05	31.60	21.45	21.44
			Perchloric acid	C ₁₈ H ₁₈ OC·ClO ₄ ^d				27.90 27.98
3	Phenylthioxanthenyl- ^a	180	Zinc chloride ^b	C ₁₈ H ₁₈ SCCl·ZnCl ₂	23.91	24.11	14.69	14.75
			Ferric chloride	C ₁₈ H ₁₈ SCCl·FeCl ₃	30.11	30.18	11.86	11.83
			Stannic chloride	C ₁₈ H ₁₈ SCCl·SnCl ₄	31.15	31.09	20.85	20.22
4	Phenyl-di- β -naphthoxan- thene- ^a	202	Zinc chloride	C ₂₆ H ₁₇ OC·ZnCl ₂	20.11	19.99	12.36	12.15
			Stannic chloride	C ₂₆ H ₁₇ OC·SnCl ₄	27.14	26.90	18.17	17.67
5	12-Phenyl-12- β -benzoxan- thene- ^{a,c,e}	191	Zinc chloride	C ₂₂ H ₁₆ OC·ZnCl ₂	22.21	22.15	13.65	13.43
			Ferric chloride	C ₂₂ H ₁₆ OC·FeCl ₃	28.09	27.84	11.06	11.05
			Stannic chloride	C ₂₂ H ₁₆ OC·SnCl ₄	29.39	29.23	19.68	19.39
			Perchloric acid	C ₂₂ H ₁₆ OC·ClO ₄ ^{d'}				24.48 24.44
6	Tri- <i>p</i> -anisylmethyl- ^a	162	Ferric chloride	(CH ₃ OC ₆ H ₄) ₃ CCl·FeCl ₃	26.71	26.59	10.52	10.62
7	Diphenyl- α -naphthyl-	187	Zinc chloride	11-Phenylcrysofluorene, colorless				
8	Phenylbiphenyl- α -naph- thyl-	118	Zinc chloride } Ferric chloride }	{ 11-Biphenylchrysofluorene (formula IV) m. p. 276°, colorless { (8,11-Biphenylchrysofluorene (formula V) m. p. 190°, colorless				

^a The carbinol chloride-hydrochloride was combined with thioglycolic acid (Ref. 4c). ^b This gave a yield of only 25%, due to solubility of the halochromic salt in acetic acid. ^c This compd. has been since described by Wallis and Adams Ref. 4c. ^d and ^{d'} M. p. 282 and 260°, respectively. ^e Carries one molecule of acetic acid of crystallization, m. p. 112°.

results are summarized in Table I, experiments 1 to 6 inclusive.

In two experiments with phenylxanthenylthioglycolic acid (No. 2 in Table I), allowing fair amounts of this compound to react with perchloric acid and with zinc chloride, it was established definitely that the filtrates

α -naphthylmethylthioglycolic and with the phenylbiphenyl - α - naphthylmethylthioglycolic acids (Table I, experiments 7 and 8).

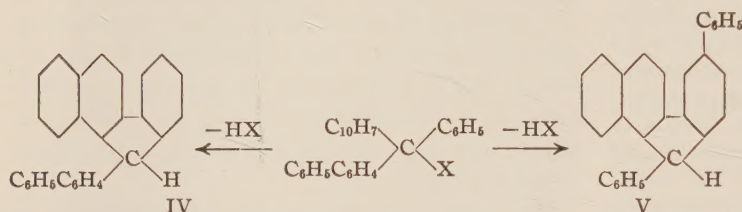
(11) Rosenheim and Davidson, *Z. anorg. Chem.*, **41**, 237 (1904).

(12) Ullmann and Mourariew-Winogradoff, *Ber.*, **38**, 2213 (1905).

(13) Schoepfle, *THIS JOURNAL*, **44**, 188 (1922).

When to an acetic acid solution of the former compound zinc chloride or ferric chloride is added, a red color is developed which gradually becomes lighter. After several hours at room temperature, the color fades and there separates the 11-phenylchrysofluorene described by Ullmann, with a yield of 45%.

Phenylbiphenylnaphthylmethylthioglycolic acid behaves toward metal halides similarly. The intense blue color which is initially developed on the addition of zinc or ferric chloride, gradually becomes lighter, white crystals begin to separate, and the change is practically complete after some twenty-four hours at room temperature. In this instance fluoreneation probably takes two distinct directions



The 11-biphenylchrysofluorene (IV), m. p. 276°, has been described previously by Dilthey.¹⁴ It was obtained by us in 36 and 31% yields in the experiments with zinc chloride and ferric chloride, respectively. The second compound, m. p. 190°, was obtained in 54% yield, and requires further confirmation of its probable constitution (V).

The cleavage by the metal halides and subsequent fluoreneation is characteristic not only of the racemic variety, but equally so, of course, of the optically active antipodes. A sample of the *l*-antipode was prepared according to Wallis' directions and had a specific rotation $[\alpha]_D^{25} -12.88^\circ$ (1.025 g. in 25 cc. of carbon tetrachloride, in 1-dm. tube; rotation -0.52°). After 48 hours of standing, the deep color of the zinc chloride double salt completely vanished and there was obtained from the acetic acid solution the fluorene IV in 45% yield. It showed no measurable rotation.

It should be mentioned that when a naphthyl group is at the same time a part of a xanthone ring, fluoreneation is not induced.

Optical Evidence of the Cleavage Process in Phenylbiphenylnaphthylmethylthioglycolic Acid.—Since, for the reasons mentioned above, no crystalline double salt could be isolated in the reaction of that compound with metal halides, the attempt was made to prove, by means of absorption spectra, the formation and temporary existence of the surmised double salt.

The general procedure followed was as described by Anderson and Gomberg.¹⁵ The solutions were made up to have a suitable intensity of color and the absorption was measured as quickly as possible in order to avoid much decrease in color due to the ensuing fluorene formation. The following concentrations were found suitable for use: (1) 27.5 mg. of phenylbiphenylnaphthylchloromethane in

benzene plus 20 mg. of zinc chloride in 7 cc. of ether, diluted to 25 cc. with benzene; (2) 0.2 g. of the thioglycolic acid derivative in benzene plus 0.139 g. of zinc chloride in 7 cc. of ether, diluted to 25 cc. with benzene; (3) 2.8 mg. of the carbinol in acetic acid plus 0.015 cc. of 70% perchloric acid, diluted to 25 cc. with acetic acid; (4) 6.0 mg. of the thioglycolic acid derivative in acetic acid plus 0.03 cc. of 70% perchloric acid, diluted to 25 cc. with acetic acid.

On Plate I are shown the curves obtained by adding zinc chloride to the ether-benzene solution of (1) the chloromethane and (2) the thioglycolic acid derivative. It is seen that the curves are very similar and that the peaks of the absorption bands occur at exactly the same frequency number. The substance producing the color must have the same structure in each case—it is the double salt carbinol chloride-zinc chloride. The difference in the height of the absorption bands indicates that the quantity of colored material is, roughly, 4:1 in favor of the chloromethane. And yet, in comparing these curves it must be borne in mind that the fluorene formation proceeds faster in the case of the carbinol chloride solution, as was clearly indicated by the fact that this solution faded in color quite rapidly, while the solution of the thioglycolic acid derivative remained of the same color intensity for a much longer time. The difference may be explained on the assumption that, the cleaving effect being slow, only a comparatively small amount of the double salt is produced in a given period of time. On the same Plate I are shown the curves obtained when (3) the carbinol and (4) the thioglycolic acid compound were treated with perchloric acid. It will be noted that these curves are practically identical in every respect. The causative agent of the color is in both cases phenylbiphenylnaphthylmethyl perchlorate and is present in substantially the same amount. The cleavage here must be occurring rapidly.

One may now venture to offer a plausible explanation concerning the perplexing nature of the results in Wallis' experiments with phenylbiphenylnaphthylmethylthioglycolic acid. In order to minimize any possible racemizing effect of the halochromizing agents upon the triaryl-methyl compound, the reactants in his experiments were each precooled and the mixtures were hydrolyzed at once. But even these limiting conditions did not hinder cleavage of the compound

(14) Dilthey, *J. prakt. Chem.*, **109**, 320 (1925).

(15) Anderson and Gomberg, *This Journal*, **50**, 203 (1928).

by the agents sulfuric or perchloric acid, or mercuric chloride.¹⁶ In the experiments, however, when zinc chloride and ferric chloride were used, the cleavage effect under these particular circumstances was presumably only slight, and yet

creases in the optical rotation of the samples, in his two quantitative experiments with zinc chloride and with iron chloride, may indicate either a cleavage to the extent of about 4%, or they may be due largely to unavoidable experimental errors.

9-Phenylfluorenylthioglycolic Acid and Perchloric Acid or Zinc Chloride.—The chlorine atom in 9-phenylfluorenyl chloride is known to be bound to the central carbon atom more strongly than in other triarylmethyl chlorides. Moreover, 9-phenylfluorenyl is known to exist almost entirely in the form of the hexa-arylethane compound and to absorb oxygen only with difficulty.¹⁷ In harmony with these facts it has now been found that the C-S bond here is not readily ruptured. 9-Phenylfluorenylthioglycolic acid (m. p. 149°) does not produce any, or but a faint, color when treated with zinc chloride or with perchloric acid in acetic acid, or in ether solution. Accordingly, after several hours of standing at room temperature, the unchanged thioglycolic acid derivative was recovered in 94 and 98% yields, respectively.

It remains to be determined whether with longer time or higher temperature cleavage in this and other fluorenyl derivatives can be made to ensue. However, from the limited evidence now at hand, it would seem that if a triarylmethylthioglycolic acid is not cleaved by the metal halide, then the halochromic effect does not ensue.

Summary and Conclusions

1. The action of perchloric acid and of certain metal halides upon seven new and two previously described triarylmethylthioglycolic acids has been studied. It has been found that the primary reaction is to split the molecule between the central carbon atom and the sulfur atom, forming a triarylmethyl perchlorate or halide, and either free thioglycolic acid or a salt of this acid. In general, this primary action is followed by a further reaction between the triarylmethyl halide with a second molecule of the metal halide resulting in the formation of a colored double salt, $R_3CCl \cdot MeCl_n$.

2. When the thioglycolic acid derivative contains a naphthyl group attached to the central carbon atom, a still further reaction may also occur, which involves the removal of a molecule of hydrogen chloride from the triarylmethyl halide produced, and then a fluorene derivative is formed.

3. From the absorption spectra of solutions containing phenylbiphenyl- α -naphthylmethylthioglycolic acid and zinc chloride, or perchloric acid, evidence has been adduced which indicates that the halochromic compounds initially formed are not, as had been postulated by Wallis, merely addition products of the thio compound with the

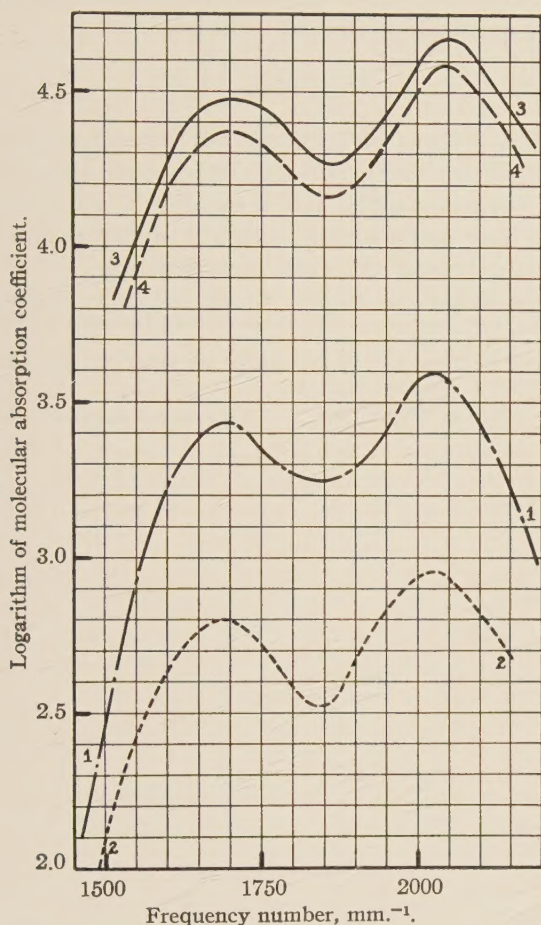


Fig. 1.—Absorption spectra of solutions of halochromic salts from phenylbiphenyl- α -naphthylmethylthioglycolic acid: Curve 1, phenylbiphenyl- α -naphthylchloromethane with zinc chloride in ether-benzene solution; Curve 2, phenylbiphenyl- α -naphthylmethylthioglycolic acid with zinc chloride in ether-benzene solution; Curve 3, phenylbiphenyl- α -naphthylcarbinol with perchloric acid in glacial acetic acid solution; Curve 4, phenylbiphenyl- α -naphthylmethylthioglycolic acid with perchloric acid in glacial acetic acid solution.

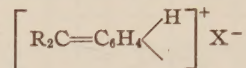
enough of the intensely halochromic salt, $R_3CCl \cdot MeCl_n$, was produced to impart to the solution deep color. Upon hydrolysis of these mixtures most of the original *l*-triarylmethylthioglycolic acid was recovered as such. The recorded de-

(16) Holmberg, *J. prakt. Chem.*, **135**, 57 (1932), found mercuric chloride to be the best agent for splitting quantitatively mercaptol-acetic acid and other similar compounds.

(17) Gomberg and Cone, *Ber.*, **39**, 1469 (1906); Schlenk, *et al.*, *ibid.*, **43**, 1783, 3541 (1910).

halochromizing agent, but that here, also, cleavage of the thio compound ensues first and is followed by the formation of the colored derivatives $R_3C \cdot X$ ($X = ClZnCl_2$, or ClO_4). Because of the naphthyl group in the molecule, these salts gradually undergo further change into colorless fluorene derivatives. It is now inferred that Wallis' conclusions concerning the nature of the halochromic derivatives were based on experimental evidence misleading in nature. When reinterpreted in the light of the evidence presented in this paper, his results do not preclude for the halochromic compounds a quinonoid structure, these results being equally consistent with that or with the carbonium-ion constitution of these derivatives. Both structures predicate carbinol formation on hydrolysis, and racemization, in the process: colorless triarylcarbinol derivative $\rightarrow$ halochromization $\rightarrow$ carbinol.

4. The advantages, however, of the quinonoid hypothesis concerning the constitution for the substances under discussion are becoming generally recognized and with various slight modifications that constitution is being accepted.¹⁸ The constitution as originally proposed,¹⁹ namely, the *quinocarbonium salt* structure



takes account of both concomitant phenomena, the salt-character and the chromogenic character of the compounds, and is capable of accounting for their many strictly chemical properties which would remain otherwise unexplainable.

(18) Hantzsch and Burwoay, *Ber.*, **64**, 1622 (1931); Burwoay, *ibid.*, 1635; Lifschitz, *Zeits. wissents. Photogr., Photophys. u. Photochem.*, **32**, 131 (1932).

(19) Gomberg, *Ber.*, **40**, 1847 (1907); **42**, 406 (1909); *Ann.*, **370**, 142 (1909); **376**, 183 (1910).

ANN ARBOR, MICHIGAN

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